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(72) Inventors ALFRED ANISIMOVICH BERLIN
TAMARA YAKOVLEVNA KEFELI
NINA VASILIEVNA VARLAMOVA
GRIGORY MIKHAILOVICH STRONGIN
JUDIF MARKOVNA ALTSHULER
BORIS IVANOVICH KOLOMAZOV and
ALEXEI VASILIEVICH EFIMOV

(54) OLIGOURETHANACRYLATES, METHODS FOR THEIR MANUFACTURE AND POLYMERS ON THE BASIS THEREOF

(71) We, ORDENA LENINA INSTITUT KHIMICHESKOI FIZIKI AKADEMII NAUK SSSR, 2-b Vorobievskoe shosse, Moscow, Union of Soviet Socialist Republics (USSR) and CHERNORECHENSKY DVAZHDY ORDENA TRUDOVOGO KRASNOGO ZNAMENI KHIMICHESKY KOMBINAT IMENI M. I. KALININA, oblast Gorkovskaya, Dzerzhinsk, USSR—both State Enterprises organised and existing under the laws of USSR, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a new group of polymerisable oligourethanacrylates, to the methods for preparing same and to polymers made therefrom.

Polyurethanes are very important materials in the manufacture of various polymers and articles.

Because of their unique combination of high physico-chemical properties, good resistance to attrition, stability against the action of many solvents, oxidants, water, oils and fuels, high adhesive strength with respect to various materials, and many other valuable properties, polyurethanes are used on an ever increasing scale in the manufacture of elastomers, foams, protective coatings, glues, sealing compounds and other polymeric materials.

A wide range of starting materials can be used in the manufacture of polyurethanes; this makes it possible to prepare polyurethanes having varied structures and different numbers of cross links, to vary the flexibility of its macromolecules, the character of the intermolecular interaction, and thus to obtain materials possessing desired properties.

The method most widely used in the manufacture of polyurethanes is a polycondensation reaction between low-molecular weight or oligomeric di- or polyisocyanates and alkyleneglycols of carbo- or heterochain diols or polyols of various structures.

If bifunctional components are used, polyurethanes of linear structure are formed. An increase in the number of functional groups to three or more results in branched or reticulate polyurethanes. The formation of polyurethanes by this method proceeds according to the mechanism of migration polymerization.

A previously proposed method of preparing reticulate polyurethanes, involves combining the interaction between isocyanates and glycols or their monosubstituted derivatives with the reaction of radical polymerization of vinyl compounds, which ensure increased thermal stability and improve some mechanical properties of the polymers. According to such a method of preparing reticulate polyurethanes, first oligomeric compounds containing urethane groups and unsaturated polymerizable groups are synthesized, for example, by the interaction between oligoetherglycols and oligoesterglycols or oligodienediols with diisocyanates and the monomethacrylic ether of ethyleneglycol, or by the interaction between oligoglycols with vinyl monomers containing isocyanate groups. The oligomeric compounds thus prepared are then polymerized according to the radical mechanism with the formation of polyurethanes having reticulate structure.

The main disadvantage of the above-mentioned methods for preparing polyurethanes is the use of isocyanates which are necessary to form urethane bonds.

The formation of urethane with the use of isocyanates is usually accompanied by side reactions which produce allophanic and biuret groups possessing low thermal and oxidation stability, and which are incapable of bearing stress, and hence impair the properties of the polyurethanes produced.

Most aliphatic and aromatic isocyanates are toxic compounds and therefore special precautions have to be taken because of their high volatility.

A restricted number of representatives of the aliphatic and aromatic isocyanates produced on an industrial scale makes it impractical to vary widely the structure, and hence, the properties of polyurethanes produced from such compounds.

Moreover, the method for preparing isocyanates having practical importance, are labour-consuming and consist of several steps (for example, separation and purification of isomers in the synthesis of toluylenediisocyanates), and this raises the cost of these products.

According to the present invention there is provided an oligourethanacrylate having the general formula I

$$[CH_2{=}C(X){-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}R{-}U]_pR'$$

in which

X is a hydrogen or halogen atom or a methyl group;

R is an alkylene or arylene group;

p is an integer and is 2 or 3 or 4 depending on the valency of R′;

U is a urethane group of formula V or VIII

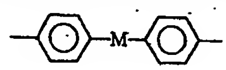
$$-N(Y){-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O-$$

or

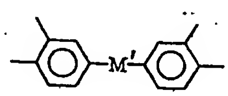
$$-O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}N(Z)-$$

in which Y is hydrogen or an aryl group and Z is hydrogen, an alkyl or an aryl group;

R′ is a divalent, trivalent or tetravalent group, the said divalent group being selected from alkylene groups of from 2 to 10 carbon atoms, phenylene groups, dimethyl-substituted phenylene groups, a diphenylene group, the group of formula IX



in which M is CH_2, O, S, SO_2, NH or $(CH_3)_2C$, divalent aliphatic groups containing one or two ether groups or an ester group, the said trivalent group being a trivalent aliphatic hydrocarbon group, and the said tetravalent group being a tetravalent aliphatic hydrocarbon group or the group of formula XII



where M′ is a methylene or an oxygen atom: optionally the group R′ may be an oligomeric group of formula

$$R'''{-}[{-}U{-}R''{-}U{-}R''']_n$$

in which R″ is any one of the divalent groups defined hereinabove in respect of R′, U is as defined hereinabove, R‴ is one of the divalent or trivalent groups defined hereinabove in respect of R′, n is an integer of 1 to 5 when R‴ is divalent and n is 1 when R‴ is trivalent.

Further according to the present invention there is provided a method of preparing an oligourethaneacrylate of general formula I, comprising reacting a polyol poly-

chloroformate with a telogen of formula IV, or reacting a polyamine with a telogen having the formula III

$$CH_2{=}C(X){-}\overset{\overset{O}{\|}}{C}{-}O{-}R{-}O{-}\overset{\overset{O}{\|}}{C}{-}Cl \qquad \text{III}$$

$$CH_2{=}C(X){-}\overset{\overset{O}{\|}}{C}{-}O{-}R{-}N(Y)H \qquad \text{IV}$$

in which X, Y and R are a defined above, said reaction being carried out in organic solvent medium in the presence of a hydrogen chloride acceptor and at a temperature of from minus 10°C to the boiling point of the solvent.

The method according to the invention may be carried out in two alternative manners, namely

(a) the reaction of the components is carried out according to the invention in a medium of an organic solvent at a temperature within the range from minus 10°C to the boiling point of the particular solvent used, and

(b) the method is realized, according to the invention, in a water-organic solvent system at room temperature.

The polymerizable oligourethanacrylates characterised by the above formula I contain in their molecules urethane groups and polymerizable terminal or regularly arranged ethylenically unsaturated bonds. The unsaturated ethylenic bonds are introduced into the oligourethanacrylates together as part of the telogens.

The telogens are compounds which contain in their molecules a terminal unsaturated group which is capable of polymerisation and also contain a functional amine group or chloroformate group which participates in the process of condensation. The telogens are compounds having the formula III or IV.

$$CH_2{=}C(X){-}\overset{\overset{O}{\|}}{C}{-}O{-}R{-}O{-}\overset{\overset{O}{\|}}{C}{-}Cl \qquad \text{III}$$

or

$$CH_2{=}C(X){-}\overset{\overset{O}{\|}}{C}{-}O{-}R{-}N(Y)H \qquad \text{IV}$$

where R, X and Y are as defined above.

The term "monoacrylate" as used herein means an ester containing one acrylate group per molecule and is used generically to describe an ester of not only acrylic acid itself but of homologues such as methacrylic acid and halogenated acids such as monohaloacrylic acid.

The telogen of formula III is a chloroformate of an alkyleneglycol monoacrylate or a bis-phenol and may be, for example, the chloroformate of the monoacrylic, monomethacrylic or monohalo-acrylic ester of ethyleneglycol, diethylene glycol, triethyleneglycol, propyleneglycol-1,3: butyleneglycol-1,4; pentamethyleneglycol-1,5; diphenylolpropane, resorcinol or hydroquinone.

The telogen containing the functional amino group (formula IV) is a monoaminoalkyl acrylate or an N-aryl substituted monoaminoalkyl acrylate containing not less than one hydrogen atom at the nitrogen atom, for example, 2-aminoethylacrylate, 2-aminoethylmethacrylate and 2-phenylaminoethylmethacrylate.

The urethane groups of oligourethanacrylate are formed as a result of a condensation reaction between the functional chloroformate group of either the polyol polychloroformate or the telogen of formula III with the amino groups of the polyamine or by condensation of the chloroformate group of the polyol polychloroformate with the amine group of the telogen of formula IV.

If the telogen contains the functional group —N(Y)H (formula VI) and reacts with the chloroformate group of the polyol polychloroformate urethane group of the oligourethanacrylate has the structure

$${-}N(Y){-}\underset{\underset{O}{\|}}{C}{-}O{-}$$

(formula V), Y being as defined above.

If the telogen contains the functional chloroformate group —O—CO—Cl (formula VIII) and reacts with the amino group of polyamine, the urethane group of the oligourethanacrylate has the structure

$$-O-\overset{\overset{\displaystyle O}{\|}}{C}-N(Z)-$$

(formula VIII) where Z is as defined above.

The polyol polychloroformate may be the bischloroformate of ethyleneglycol, diethyleneglycol, triethyleneglycol, propyleneglycol, butyleneglycol, pentamethyleneglycol, hexamethyleneglycol, octamethyleneglycol, decamethyleneglycol, polyoxyethyleneglycol, polyoxypropyleneglycol, diphenylolpropane, resorcinol or hydroquinone or the trichloroformate of etriol, or glycerol or tetrachloroformate pentaerythritol. The polyamines used in the method are for example ethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, octamethylenediamine, decamethylenediamine, metaphenylenediamine, para-phenylenedimine, 4,4′-diaminodiphenylmethane, benzidine, 4′,4′-diaminodiphenylamine, 4,4′-diaminodiphenylsulphide, 4,4′-diaminodiphenylsulphone, 4,4′-diaminodiphenyloxide, meta-xylylenediamine, para-xylylenediamine, 3,3′,4,4′-tetraaminodiphenylmethane and 3,3′4,4′-tetraaminodiphenyloxide.

The above-mentioned polyol polychloroformates and the polyamines determine the character of the hydrocarbon radicals located between the urethane groups in oligourethanacrylates and expressed by the radical R′ and R″ and in the general formula.

The size of these radicals, and also the degree of polycondensation 'n' of the oligourethanacrylate when R′ is the group $R'''-[-U-R''-U-R''']_n$ determines its molecular weight and physico-chemical properties.

'n' can be one or any integer greater than one.

For bifunctional components (bis-chloroformates of glycols and bis-phenols or diamines), the magnitude of 'n' if $R'''-[-U-R''-U-R''']_n$ is present should be from 1 to 5.

For the polyfunctional components, where the number of functional chloroformate or amino groups is 3 or 4, the value of 'n' should be 1.

By varying the size of the radicals R′ and R″, and also the magnitude 'n', oligourethanacrylates of various molecular weights can be produced.

For example, when $R'''-[-U-R''-U-R''']_n$ is absent, and the telogen contains the functional amino group, oligourethanacrylates with high molecular weights can be obtained on account of using bis-chloroformates of polyols in which R″ is a high-molecular weight radical of a bifunctional oligoether or oligoester, for example, a radical of polyoxypropyleneglycol, polyoxyethyleneglycol or polyalkyl oligoester on the basis of dicarboxylic acids and glycols.

Increasing the size of the radical R, R′ and R″ at constant value of 'n', or increasing the value of 'n' at constant size of the radicals, results in an increase in the molecular weight of the oligourethanacrylate formed.

Depending on the nature and structure of the starting compounds, and also on the degree of polymerization (n), oligourethanacrylates are non-volatile colourless or faintly coloured liquids having no specific odour, of variable viscosity, or colourless relatively low-melting crystalline substances readily soluble in various monomers and polymerizable oligomers of vinyl, and allyl types, and also in most organic solvents. Interesting representatives of oligourethanacrylates, prepared by the proposed method are the following oligomeric compounds:

1.

$$CH_2=CH-COOCH_2CH_2NHCOO(CH_2)_4OOCNHCH_2CH_2OOC-CH=CH_2 \quad \text{(XIII)}$$

2.

$$CH_2=C(CH_3)-COOCH_2CH_2OOCNH(CH_2)_2NHCOOCH_2CH_2OOC-C(CH_3)=CH_2 \quad \text{(XIV)}$$

3.

$$CH_2=C(CH_3)-COOCH_2CH_2OOCNH(CH_2)_{10}NHCOOCH_2CH_2OOC-C(CH_3)=CH_2 \quad \text{(XV)}$$

4.

$$CH_2{=}C(CH_3)COOCH_2CH_2N(C_6H_5)COO(CH_2)_2OOCNHCH_2CH_2OOC{-}C(CH_3){=}CH_2$$

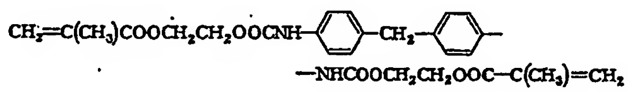
(XVI)

5.

$$CH_2{=}C(CH_3)COOCH_2CH_2NHCOO(CH_2)_2O(CH_2)_2O(CH)_2OOCN(C_6H_5)CH_2CH_2OOC{-}C(CH_3){=}CH_2$$

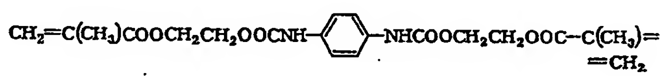
(XVII)

6.



(XVIII)

7.



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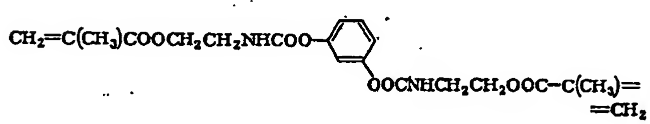
8.



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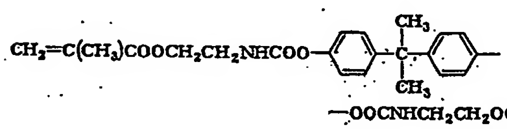


(XXI)

10.

$$CH_3CH_2{-}C(CH_2OOCNHCH_2CH_2OOC{-}C(CH_3){=}CH_2)_3$$

$$\begin{array}{l} \quad\quad\quad\;\; CH_2OOCNHCH_2CH_2OOC{-}C(CH_3){=}CH_2 \\ \quad\quad\quad\;\; | \\ CH_3CH_2{-}C{-}CH_2OOCNHCH_2CH_2OOC{-}C(CH_3){=}CH_2 \\ \quad\quad\quad\;\; | \\ \quad\quad\quad\;\; CH_2OOCNHCH_2CH_2OOC{-}C(CH_3){=}CH_2 \end{array}$$

(XXII)

11.

$$CH_2{=}C(CH_3){-}COOCH_2CH_2OOCNH(CH_2)_2NHCOO(CH_2)_2O(CH_2)_2OOCNH(CH_2)_2{-}NHCOOCH_2CH_2{-}OOC{-}C(CH_3){=}CH_2$$

(XXIII)

The proposed polymerizable oligourethanacrylates may be prepared by two alternative methods.

According to the first version, the polyol polychloroformate or the polyamine is reacted with the appropriate telogen in an organic solvent medium in the presence of an organic base which is a hydrogen chloride acceptor which accepts HCl evolved in the reaction, at temperatures within a range of from minus 10°C to the boiling point of the particular solvent used in the reaction. The preferable range of process temperatures is from minus 10°C to +80°C. The process may be effected under atmospheric pressure in an anhydrous solvent with vigorous stirring of the reactants in the absence of any inhibitors of the pre-polymerization process. The condensation reaction may take 4—5 hours. The yield of the oligourethanacrylate in the described version of the method is about 85—90 per cent of theory.

According to the second version, the polyol polychloroformate or polyamine is reacted with the appropriate telogen under conditions of inter-phase condensation in a

water-organic solvent system in the presence of an organic base or an inorganic alkaline agent, i.e., a hydrogen chloride acceptor, at room temperature.

The process is preferably carried out under atmospheric pressure in the absence of inhibitors of polymerization and with intensive stirring of the reaction mixture which is formed by adding a solution of the chloroformate of the telogen or the polyol in an anhydrous organic solvent to an aqueous solution of diamine containing the hydrogen chloride acceptor. The volume ratio of the aqueous phase to the organic phase should preferably be 1:1. The condensation reaction takes 15—30 minutes. The yield of oligourethanacrylates in this version of the method is 90—95 per cent of theory.

The reactants, viz., telogens, polyamines and polychloroformates of polyols, may be introduced into the reaction mixture either consecutively or simultaneously.

In stepwise addition of the components, oligourethanacrylates having molecular weights varying with a narrow range may be obtained.

The ratio between the quantities of polyol polychloroformate and polyamine (with accounting for the number of the functional groups in these components) depends on the particular telogen and the value of "n".

Thus, when n=0, oligourethanacrylates are prepared as a result of condensation of a telogen with one of the said reactants. If the telogen contains the chloroformate functional group, it is reacted with a polyamine, and if the telogen contains the amine functional group, a polyol polychloroformate is added to the reaction mixture to react with the telogen.

The components are preferably taken in stoichiometric quantities. For example, if n=0, the molar ratio of the telogen to the bifunctional component diamine or bis-chloroformate of glycol or bis-phenol is 2:1, and to the tetrafunctional component tetramine or tetraol, 4:1.

The resultant products can be oligourethanacrylates of the following structure:

$$R'\text{—}[\text{—}U\text{—}R\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\text{—}C(X){=}CH_2]_p \qquad \text{(XXIV)}$$

where: R, R′ and X are as defined hereinabove.

p is the number of the functional groups in the component reacting with the telogen, which determines the required quantity of the telogen.

If n is 1, and one or both components (polyamine or polyol) are bifunctional compounds, their amount is determined by the molar ratio

$$\frac{n}{n+1}$$

where n corresponds to the quantity of the component having the same functional group as in the telogen. If one or two components have more than two functional groups, the ratio of the components is determined from the stoichiometric reaction. For example, oligourethanacrylate characterized by the formula:

$$\begin{array}{ccc} CH_2{=}C(X)\text{—}COO\text{—}R\text{—}U & & U\text{—}R\text{—}COO\text{—}C(X){=}CH_2 \\ \diagdown & & \diagup \\ & R'''\text{—}U\text{—}R''\text{—}U\text{—}R''' & \\ \diagup & & \diagdown \\ CH_2{=}C(X)\text{—}COO\text{—}R\text{—}U & & U\text{—}R\text{—}COO\text{—}C(X){=}CH_2 \end{array}$$

(XXV)

where: n is 1 and X, R, R″ and R‴ are as defined hereinabove is prepared by the interaction between a diamine and a triol trichloroformate taken at a ratio of

$$\frac{n}{n+1}$$

respectively, and a telogen having the functional amino group in an amount required to form the compound of the above formula. If the components are introduced, simultaneously, oligourethanacrylates, which are actually the closest telomer homologues, are obtained.

Acceptors for the hydrogen chloride evolved in the reaction may be tertiary amines, e.g. trimethylamine, triethylamine, tributylamine, pyridine, pyridine homologues, N,N-diethylaniline and N,N-dimethylaniline; these may be used in the first version of the method.

In the second version, the choice of hydrogen chloride acceptors is wider. It includes organic bases and inorganic alkaline agents, such as pyridine, oxides, hydroxides or carbonates of alkali or alkaline-earth metals, for example potassium hydroxide, sodium hydroxide, sodium carbonate and potash.

The organic solvents which are most suitable for the purpose are for example, chloroalkanes, nitroalkanes, benzene and benzene homologues and tetrahydrofuran. Particularly useful are methylene chloride, dichloroethane, trichloroethylene, nitrobenzene, nitromethane, dimethylformamide, benzene and toluene.

The method for preparing oligourethanacrylates according to the first version may be carried out in a reaction vessel provided with a stirrer, a thermometer, a reflux condenser and a dropping funnel. The organic solvent, the amine component and a hydrogen chloride acceptor are loaded into the reaction vessel. The contents may be cooled on a bath containing a cooling mixture to a temperature of minus 10°C and then the chloroformate component in the same organic solvent may be added gradually. The components may be reacted with vigorous stirring the reaction mixture, the temperature being maintained within a range of from minus 10°C to a minus 5°C. When all the chloroformate component has been added, the temperature of the reaction mixture may be raised to the boiling point of the solvent (or somewhat lower) and the reaction mixture kept at this temperature for 3—4 hours. On termination of the reaction the mixture is preferably cooled to room temperature, and treated with a 5 per cent solution of hydrochloric acid. The organic layer which separates may be washed with water to a neutral reaction and until free of chloride ion, dried over calcined sodium sulphate and filtered. The solvent may then be distilled off under a residual pressure of 1—2 mm Hg.

According to the other version, the oligourethanacrylates may be prepared in a reaction vessel into which an aqueous solution of the amine component and a hydrogen chloride acceptor are placed. Then, the solution of the chloroformate component in an organic solvent may be added to the reaction mixture with vigorous stirring at room temperature. The aqueous layer is preferably decanted, and the remaining organic layer washed with water to neutral reaction. The solvent may then be distilled off at a residual pressure of 1—2 mm Hg. If the compounds are crystalline, the organic solvent may be removed by distillation after decantation of the aqueous layer. The still residue is preferably washed with water until no chloride ion is detected in the filtrate and dried under vacuum or in a dessicator over concentrated H_2SO_4.

The method for preparing oligourethanacrylates in either of the two versions can be realized with simultaneous and consecutive introduction of the reactants. In the latter case provision may be made for isolating an intermediate oligomeric compound from the reaction mixture for the purpose of subsequent condensation with a corresponding telogen. The condensation of the intermediate oligomeric compound with the telogen can be carried out immediately or later.

Unlike the first version of the method for preparing oligourethanacrylates, the second version is more advantageous from the technical point of view and with respect to the yield. The advantages of the second version are 1) the possibility of using polyamines in the form of salts, for example their salts with HCl, HBr and H_2SO_4 and their trichlorohydrates, which are less toxic, more stable and purer compounds; 2) the possibility of using inorganic alkaline hydrogen chloride acceptors; 3) carrying out the reactions at room temperature in a water-organic solvent system, at high reaction rates between the reactants without using any external source of energy. The proposed method in two versions considerably widens the range of raw materials that can be used in the manufacture of relatively cheap readily polymerizable oligourethanacrylates and the range of the oligourethanacrylates themselves.

The conditions under which the two versions can be realized exclude resinification and ensure the preparation of faintly coloured or colourless oligourethanacrylates with high yields. One of the advantages of the present invention is the preparation of new polymerizable oligomeric compounds containing in their molecules urethane groups obviating the use of isocyanates, which, in turn, rules out the formation of undesired unstable allophanic and biuret bonds and improves the service properties of polyurethanes on their basis.

The specific feature of the herein proposed method is also the feasibility of oligomerization of oligourethanacrylates, viz., the controlled preparation of oligourethanacrylates having various molecular weights, length and flexibility of the oligomeric

molecule in accordance with the predetermined polycondensation coefficient n. Oligourethanacrylates may be oligomerized in the reaction of non-equilibrium condensation by adjusting the ratios of the reacting polyfunctional components to the telogen with a simultaneous (the condensation telomerization principle) or separate introduction of the reactants into the reaction mixture. Oligourethanacrylates are capable of trimeric polymerization and copolymerization which proceed with the formation of non-melting and insoluble products. The solidification of oligourethanacrylates is accelerated by the action of heat, light, high-energy radiation (gamma rays, fast electrons), by the initiators of free radical-chain polymerization.

Oligourethanacrylates are capable not only of homopolymerization, but of copolymerization with each other, and also with a great number of bi- and polyfunctional monomers.

The most important feature of oligourethanacrylates is their ability to polymerize on account of only terminal and regularly arranged unsaturated groups, which ensures the participation of the oligoester block of the desired type in the formation of trimeric structure of the solidified high-molecular weight polymer. This course of the process makes it possible to transfer the main properties of the oligoester into the corresponding reticulate polymer, which ensures the preparation on the basis of oligourethanacrylates of polymeric materials possessing the required structure and the desired technical properties.

By changing the chemical nature of the starting components and telogens, and also the size of the oligomeric block of the oligourethanacrylates, it is possible to vary the properties of the prepared oligomers within a wide range, to change the structure of the reticulate polymers based thereon, and thus to produce the desired effect on the physico-mechanical and electric characteristics of the polymers, their resistance to heat, water, atmospheric corrosion, and other properties of the polymers.

A valuable complex of technical properties of the oligourethanacrylates is responsible for their applicability to compositions of the contact binding glass-fibre materials, colourless film-forming materials, insulating compounds, glues, various sealing materials, etc.

The invention will now be described by way of illustration in the following Examples.

Example 1

To a mixture of 0.05 mol of ethylenediamine, 0.11 mol of pyridine and 30 mol of methylene chloride cooled to $-10°C$ in a four-necked flask provided with a stirrer, a thermometer, a reflux condenser and a dropping funnel, a solution of 0.1 mol of the monochloroformate of the monomethacrylic ester of ethylene glycol in 30 ml of methylene chloride was added with vigorous stirring over a period of two hours so that the temperature of the reaction mixture did not rise above $-10°C$. After all the solution of the monochloroformiate had been added, the temperature of the reaction mixture was increased to $+43°C$ and kept under these conditions for four hours with stirring. The contents of the flask were cooled to room temperature and treated with a 5 per cent aqueous solution of hydrochloric acid. The organic layer was washed with water to neutral reaction and until free of chloride ion, dried over calcined sulphate, filtered, and the solvent distilled off under residual pressure of 1—2 mm Hg and a temperature of 25°C. The still residue was a colourless crystalline product having the following formula:

$$CH_2{=}C(CH_3){-}\overset{\overset{\displaystyle O}{\|}}{C}O{-}CH_2CH_2O\overset{\overset{\displaystyle O}{\|}}{C}NH(CH_2)_6NH\overset{\overset{\displaystyle O}{\|}}{C}OCH_2CH_2O\overset{\overset{\displaystyle O}{\|}}{C}{-}C(CH_3){=}CH_2 \quad (XIV)$$

The yield of the product is 90 per cent. M.p. 93—95°C.

Found, per cent: C, 51.37; H, 6.71; N, 7.54.
Calculated, per cent: C, 51.6; H, 6.5; N, 7.52.

Example 2

Under the conditions described in Example 1, but in dichloroethane solution 0.1 mol of the monochloroformate of the monomethacrylic ester of ethyleneglycol was reacted with 0.05 mol of hexamethylenediamine. The yield was 92 per cent. The resultant product was a colourless crystalline substance having the formula:

$$CH_2{=}C(CH_3){-}COOCH_2CH_2O\overset{\overset{O}{\|}}{C}NHCH_2CH_2NH\overset{\overset{O}{\|}}{C}OCH_2CH_2OOC{-}C(CH_3){=}CH_2$$

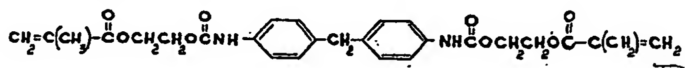
(XXVI)

The melting point of the product was 73—74°C.

Calculated, per cent: C, 56.06; H, 7.53; N, 6.54
Found, per cent: C, 56.19; H, 7.57; N, 6.62

Example 3

Under the conditions of Example 1, but in methylene chloride solution, 0.4 mol of 4,4′-diaminodiphenylmethane was reacted with 0.8 mol of the chloroformate of the monomethacrylic ester of ethylene glycol. The reaction product was a crystalline substance of the following structure:



(XVIII)

The yield of the product was 93 per cent.

Calculated, per cent: C, 63.52; H, 5.92; N, 5.49
Found, per cent: C, 63.70; H, 6.14; N, 5.83

Example 4

To a mixture of 0.1 mol of 2-aminoethylmethacrylate, 0.2 mol of pyridine and 25 ml of methylene chloride placed in a four-necked flask equipped with a stirrer, a thermometer, a reflux condenser and a dropping funnel, and cooled to −10°C, a solution of 0.05 mol of the bis-chloroformate of diethyleneglycol in 25 ml of methylene-chloride was added with stirring over a period of two hours so that the temperature of the reaction mixture did not rise above minus 10°C. When all the solution of bis-chloroformate had been added, the temperature of the reaction mixture was increased gradually to +43°C and the mixture held under these conditions for 4 hours with stirring.

The contents of the flask were then cooled to room temperature and treated with a 5 per cent aqueous solution of hydrochloric acid. The organic layer was then washed with water to neutral reaction and until free of chloride ion, dried over calcined sodium sulphate, filtered and the solvent distilled off under a residual pressure of 1—2 mm Hg and a temperature of 25°C. The still residue was a colourless viscous product. Its physico-chemical characteristics are close to theory as calculated for an oligoester having the following structure:

$$CH_2{=}C(CH_3){-}\overset{\overset{O}{\|}}{C}{-}OCH_2CH_2NH\overset{\overset{O}{\|}}{C}OCH_2CH_2OCH_2$$
$$CH_2O\overset{\overset{O}{\|}}{C}NHCH_2CH_2O\overset{\overset{O}{\|}}{C}{-}C(CH_3){=}CH_2$$

(XVI)

The yield of the product is 90 per cent.

Found, per cent: C, 51.86; H, 6.68; N, 6.65
Calculated, per cent: C, 51.92; H, 6.78; N, 6.73

Example 5

Under the conditions described in Example 4, an oligourethanacrylate was prepared from the bis-chloroformate of butyleneglycol-1,4. N,N-dimethylaniline was used as the acceptor of hydrogen chloride. The product had the following formula:

$$CH_2{=}C(CH_3){-}\overset{\overset{O}{\|}}{C}OCH_2CH_2NH\overset{\overset{O}{\|}}{C}O(CH_2)_4O\overset{\overset{O}{\|}}{C}NHCH_2CH_2O\overset{\overset{O}{\|}}{C}{-}C(CH_3){=}CH_2 \quad (XL)$$

The yield of the product was 91 per cent.

Found, per cent: C, 53.78; H, 6.99; N, 7.14
Calculated, per cent: C, 53.99; H, 7.05; N, 7.00

Example 6

Under the conditions described in Example 4, an oligourethanacrylate was prepared from the bis-chloroformate of propyleneglycol-1,3. The prepared product had the formula:

$$CH_2{=}C(CH_3){-}\overset{\overset{O}{\|}}{C}OCH_2CH_2NH\overset{\overset{O}{\|}}{C}O(CH_2)_3O\overset{\overset{O}{\|}}{C}NHCH_2CH_2O\overset{\overset{O}{\|}}{C}{-}C(CH_3){=}CH_2 \qquad \text{(XXVII)}$$

Calculated, per cent: N, 7.25; C, 52.84; H, 6.78
Found, per cent: C, 6.69; H, 6.69; N, 7.30

The yield of the product was 92 per cent.

Example 7

Under the conditions described in Example 4, an oligourethanacrylate was prepared from the bis-chloroformate of pentamethyleneglycol-1,5. The product had the following formula:

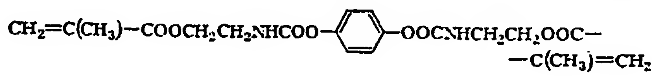
$$CH_2{=}C(CH_3){-}COOCH_2CH_2NH\overset{\overset{O}{\|}}{C}O(CH_2)_5O\overset{\overset{O}{\|}}{C}NHCH_2CH_2OOC{-}C(CH_3){=}CH_2 \qquad \text{(XXVIII)}$$

The yield of the product was 91 per cent.

Found, per cent: C, 54.98; H, 7.15; N, 6.80
Calculated, per cent: C, 55.06; H, 7.30; N, 6.76

Example 8

Under the conditions described in Example 4, an oligourethanacrylate was prepared from the bis-chloroformate of hydroquinone triethylamine being used as the acceptor of hydrogen chloride. The resultant product had the following formula:

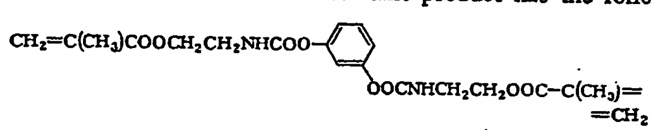

(XXIX)

The yield of the product was 90 per cent.

Found, per cent: C, 57.05; H, 5.70; N, 6.70
Calculated, per cent: C, 57.14; H, 5.75; N, 6.66

Example 9

Under the conditions described in Example 4, an oligourethanacrylate was prepared from resorcinol bis-chloroformate. The resultant product has the following formula:


(XX)

The yield of the product was 91 per cent.

Found, per cent: C, 57.01; H, 5.73; N, 6.71
Calculated, per cent: C, 57.14; H, 5.75; N, 6.66

Example 10

Under the conditions described in Example 4, an oligourethanacrylate was pre-

pared from diethyleneglycol bis-chloroformate and phenylaminoethylmethacrylate as the telogen. The resultant product had the following formula:

$$CH_2{=}C(CH_3){-}COOCH_2CH_2N(C_6H_5)COOCH_2CH_2OCH_2$$
$$CH_2OOCN(C_6H_5)CH_2CH_2OOC{-}C(CH_3){=}CH_2 \quad \text{(XVII)}$$

$n_D^{20}=1.5312$; the yield of the product was 93 per cent.

Calculated, per cent: C, 63.37; H, 6.38; N, 4.93
Found, per cent: C, 63.40; H, 6.31; N, 5.00

Example 11

Into a mixture of 1 mol of ethylenediamine, 1.1 mol of pyridine and 150 ml of methylene chloride cooled to minus 10—5°C in a four-necked flask provided with a stirrer, a thermometer, a reflux condenser and a dropping funnel, 0.5 mol of the bis-chloroformate of diethyleneglycol in 150 ml of methylene chloride was added gradually with vigorous stirring, so that the reaction temperature did not rise above zero. When all the solution of the bis-chloroformate had been added, the reaction mixture was heated gradually to 43°C and kept at this temperature with stirring for two hours. Then, to the mixture, cooled to 0°C, one mol of the chloroformate of the monomethacrylic ester of ethyleneglycol was added as described in Example 1. The reaction mixture was processed and the product isolated as described in Example 1. The resultant product had the following formula:

$$CH_2{=}C(CH_3){-}COOCH_2CH_2OOCNH(CH_2)_2NHCOOCH_2CH_2O{-}$$
$$CH_2CH_2OOCNH(CH_2)_2{-}NHCOOCH_2CH_2OOC{-}C(CH_3){=}CH_2 \quad \text{(XXIII)}$$

The yield of the product was 89 per cent.

Found, per cent: N, 9.62; C, 48.90; H, 6.40
Calculated, per cent: C, 48.81; H, 6.49; N, 9.49

Example 12

Under the conditions described in Example 4, an oligourethanacrylate was prepared from the bis-chloroformate of butyleneglycol-1,4, and 2-aminoethylacrylate as the telogen. The resultant product had the following formula:

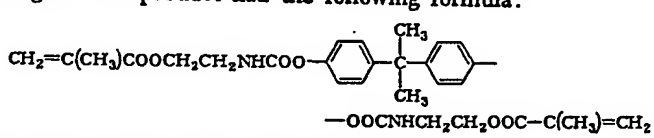
$$CH_2{=}CH{-}COOCH_2CH_2NHCOO(CH_2)_4OOCNHCH_2CH_2OOC{-}CH{=}CH_2 \quad \text{(XIII)}$$

The yield of the product was 90 per cent.

Found, per cent: C, 51.65; H, 6.56; N, 7.55
Calculated, per cent: C, 51.61; H, 6.50; N, 7.52

Example 13

Under the conditions described in Example 4, an oligourethanacrylate was prepared from the bis-chloroformate of diphenylolpropane, and 2-aminoethylmethacrylate as the telogen. The product had the following formula:



(XXI)

The yield of the product was 92 per cent.

Found, per cent: C, 64.70; H, 6.45; N, 5.26
Calculated, per cent: C, 64.67; H, 6.36; N, 5.20

Example 14

Under the conditions described in Example 4, an oligourethanacrylate was pre-

pared from the bis-chloroformate of polyoxypropylene glycol having a molecular weight of 200, and 2-aminoethylmethacrylate as the telogen. The resultant product had the following formula:

$$CH_2{=}C(CH_3){-}COOCH_2CH_2NHCO{-}\left[{-}O{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}\right]_3{-}OOCNHCH_2CH_2OOC{-}C(CH_3){=}CH_2 \qquad \text{(XXX)}$$

The yield of the product was 85 per cent.

Found, per cent: C, 55.18; H, 7.65; N, 5.69
Calculated, per cent: C, 54.97; H, 7.62; N, 5.57

Example 15

Into a flask provided with a high-speed stirrer, a thermometer, and a dropping funnel, 0.2 mol of ethylenediamine in the form of a 70 per cent aqueous solution and 0.44 mol of sodium hydroxide in 250 ml of water were charged. The mixture was cooled under intense stirring to a temperature of not above +15°C and then 0.4 mol of the chloroformate of the monomethacrylic ester of ethyleneglycol in 250 ml of anhydrous freshly distilled methylene chloride was added. The reaction mixture was stirred for 15 minutes, then allowed to stand to allow separation into two layers and the aqueous layer was decanted. The organic layer was washed with water to neutral reaction. The solvent was distilled off and the still residue was washed free of chloride ion, and dried under vacuum or in a dessicator over concentrated sulphuric acid. The resultant product was a colourless crystalline substance having the following formula:

$$CH_2{=}C(CH_3)COOCH_2CH_2OOCNHCH_2CH_2NHCOOCH_2CH_2OOC{-}C(CH_3){=}CH_2 \qquad \text{(XIV)}$$

The yield of the product was 94 per cent.

Found, per cent: C, 51.48; H, 6.51; N, 7.56
Calculated, per cent: C, 51.61; H, 6.50; N, 7.52

Example 16

Under the conditions described in Example 15, and in solution in methylene chloride, 0.2 mol of ethylenediamine hydrochloride was reacted with 0.4 mol of the chloroformate of the monomethacrylic ester of ethyleneglycol. The resultant product was a colourless crystalline substance having the following formula:

$$CH_2{=}C(CH_3)COOCH_2CH_2OOCNHCH_2CH_2NHCOOCH_2CH_2OOC{-}C(CH_3){=}CH_2 \qquad \text{(XIV)}$$

The yield of the product was 95 per cent. The assay was the same as in Example 15.

Example 17

Under the conditions described in Example 15, to a mixture of 0.2 mol of hexamethylenediamine hydrochloride and 0.88 mol of sodium chloride in 200 ml of water 0.4 ml mol of the chloroformate of the monomethacrylic ester of ethyleneglycol in 250 ml of anhydrous methylene chloride was added with intense stirring. The contents were stirred for 15 minutes. The temperature was maintained during the reaction at not above +15°C. The product had the following formula:

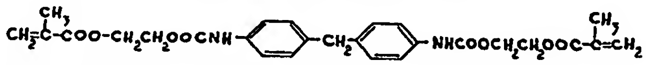
$$CH_2{=}C(CH_3)COOCH_2CH_2OOCNH(CH_2)_6NHCOOCH_2CH_2OOC{-}C(CH_3){=}CH_2 \qquad \text{(XXVI)}$$

The yield of the product was 96 per cent. The assay was the same as in Example 2.

Example 18

Under the conditions described in Example 15, 250 ml of water, 100 ml of dichloroethane, 0.44 mol of sodium hydroxide and 0.2 mol of diaminodiphenylmethane were mixed with cooling. 0.4 mol of the monochloroformate of the monomethacrylic ester of ethyleneglycol in 150 ml of dichloroethane was added. The mixing time is 30 minutes. The reaction mixture was treated and the product is isolated as described in Example 15.

The resultant product had the following formula:

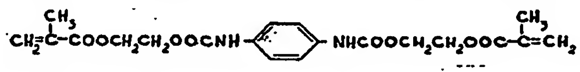


(XVIII)

The yield of the product was 99 per cent. The assay was the same as in Example 3.

Example 19

Under the conditions described in Example 15, by using sodium hydrogen carbonate as the acceptor of hydrogen chloride and in methylene chloride solution, 0.1 mol of the chloroformate of the monomethacrylic ester of ethyleneglycol was reacted with 0.05 mol of *p*-phenylenediamine. The resultant product has the following formula:



(XIX)

The yield of the product was 95 per cent.

Found, per cent:	C, 57.25;	H, 5.80;	N, 6.70
Calculated, per cent:	C, 57.14;	H, 5.75;	N, 6.66

Example 20

Under the conditions described in Example 15, to a mixture of 100 ml of water, 50 ml of methylene chloride, 0.88 mol of sodium chloride and 0.08 mol of phenylaminoethylmethacrylate cooled to a temperature of not above +15°C, 0.04 mol of the bis-chloroformate of diethyleneglycol in 50 ml of methylene chloride was added with intense stirring. The mixing time was 30 minutes. After separation of the reaction mixture into layers, the organic layer was washed with water to neutral reaction and until free of chloride ion, dried over calcined sodium sulphate, filtered, and the solvent distilled off in vacuum. The still residue was a faintly coloured viscous product having the following formula:

$$CH_2{=}C(CH_3){-}COOCH_2CH_2N(C_6H_5)COOCH_2CH_2OCH_2CH_2OOCN(C_6H_5)CH_2CH_2OOC{-}C(CH_3){=}CH_2 \quad \text{(XVII)}$$

The yield of the product is 92 per cent.

Calculated, per cent:	C, 63.37;	H, 6.38;	N, 4.93
Found, per cent:	C, 63.40;	H, 6.41;	N, 5.10

Example 21

Under the conditions described in Example 15, in a solution of dichloroethane, 0.1 mol of the chloroformate of monomethacrylic ester of ethyleneglycol was reacted with 0.05 mol of decamethylenediamine. The resultant product had the following formula:

$$CH_2{=}C(CH_3)COOCH_2CH_2OOCNH(CH_2)_{10}NHCOOCH_2CH_2OOC{-}C(CH_3){=}CH_2 \quad \text{(XV)}$$

Found, per cent:	C, 59.53;	H, 8.30;	N, 5.83
Calculated, per cent:	C, 59.49;	H, 8.32;	N, 5.78

Example 22

Under the conditions described in Example 15 and in methylene chloride solution, 0.1 mol of trichloroformiate of etriol was reacted with 0.3 mol of 2-aminoethylmethacrylate. The resultant product had the following formula:

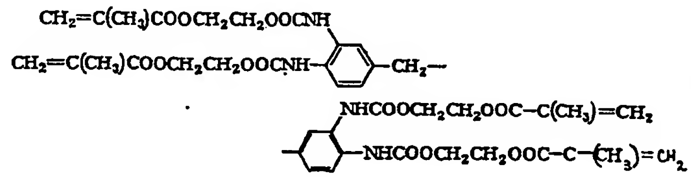
$$\begin{array}{l} \qquad\qquad\quad CH_2OOCNHCH_2CH_2OOC{-}C(CH_3){=}CH_2 \\ \qquad\qquad\quad | \\ CH_3CH_2{-}C{-}CH_2OOCNHCH_2CH_2OOC{-}C(CH_3){=}CH_2 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH_2OOCNHCH_2CH_2OOC{-}C(CH_3){=}CH_2 \end{array} \quad \text{(XXII)}$$

The yield of the product was 88 per cent.

Found, per cent: C, 54.25; H, 6.98; N, 7.10
Calculated, per cent: C, 54.08; H, 6.89; N, 7.01

Example 23

Under the conditions described in Example 18, 0.1 mol of 3,3′,4,4′-tetraaminodiphenylmethane was reacted with 0.4 mol of the chloroformate of the monomethacrylic ester of ethylene glycol. The resultant product had the following formula:



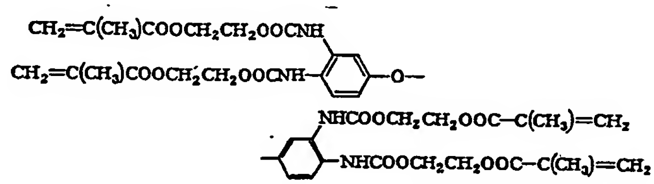
(XXXI)

The yield of the product was 82 per cent.

Found, per cent: C, 57.39; H, 6.38; N, 6.70
Calculated, per cent: C, 57.33; H, 6.34; N, 6.52

Example 24

Under the conditions described in Example 18 and in chloroform solution, 0.2 mol of 3,3′,4,4′-tetraaminodiphenyloxide was reacted with 0.8 mol of the chloroformate of the monomethacrylic ester of ethyleneglycol. The resultant product had the following formula:



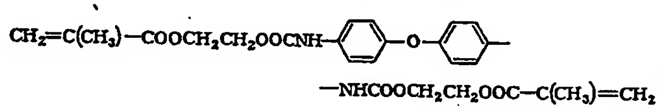
(XXXII)

The yield of the product was 84 per cent.

Found, per cent: C, 56.98; H, 6.15; N, 6.70
Calculated, per cent: C, 5687; H, 6.20; N, 6.63

Example 25

Under the conditions described in Example 18, 0.15 mol of 4,4′-diaminodiphenyloxide was reacted with 0.3 mol of the chloroformate of the monomethacrylic ester of ethyleneglycol. The resultant product had the formula:



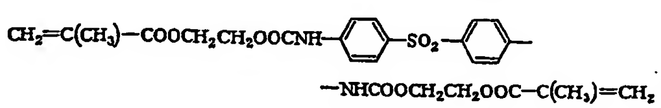
(XXXIII)

The yield of the product was 83 per cent.

Found, per cent: C, 61.19; H, 5.65; N, 5.51
Calculated, per cent: C, 60.93; H, 5.51; N, 5.46

Example 26

Under the conditions described in Example 18, 0.2 mol of 4,4′-diaminodiphenylsulphone was reacted with 0.4 mol of the chloroformate of the monomethacrylic ester of ethyleneglycol. The resultant product had the following formula:



(XXXIV)

The yield of the product was 85 per cent.

Found, per cent: C, 59.20; H, 5.46; N, 5.35
Calculated, per cent: C, 59.09; H, 5.34; N, 5.30

Example 27

An oligourethanacrylate having the formula:

$$CH_2=C(CH_3)COOCH_2CH_2N(C_8H_5)COO(CH_2)_2O(CH_2)_2COON(C_8H_5)—CH_2CH_2OOC—C(CH_3)=CH_2 \quad (XVII)$$

was polymerised by a free radical mechanism for three hours at a temperature of 90°C in the presence of 0.5 per cent of azo-bis-isobutyronitrile. The polymer was a transparent, faintly coloured non-melting and insoluble product.

Example 28

A polymer on the basis of oligourethanacrylate having the formula:

$$CH_2=C(CH_3)—COOCH_2CH_2NHCOO(CH_2)_2O(CH_2)_2OOCNHCH_2CH_2OOC—C(CH_3)=CH_2 \quad (XVI)$$

was prepared by solidification of the above compound during three hours at a temperature of 90°C in the presence of 0.5 per cent of azo-bis-isobutyronitrile. The polymer was a transparent colourless non-melting product insoluble in organic solvents.

Example 29

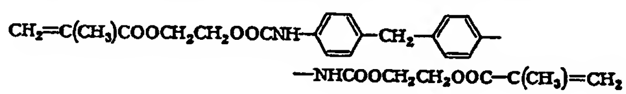
A polymer on the basis of oligourethanacrylate having the formula:

$$CH_2=C(CH_3)COOCH_2CH_2NHCOOCH_2CH_2OOCNHCH_2CH_2OOC—C(CH_3)=CH_2 \quad (XXXIX)$$

was prepared by thermal polymerization for three hours at a temperature of 120°C (solidification point). The polymer was a non-melting insoluble transparent product.

Example 30

A polymer on the basis of oligourethanacrylate having the formula:



(XVIII)

was prepared by thermal polymerisation of the above compound for three hours at a temperature of 120°C.

The solidified oligourethanacrylate was a faintly coloured transparent non-melting and insoluble product.

WHAT WE CLAIM IS:—

1. An oligourethanacrylate having the general formula 1

$$[CH_2=C(X)—\overset{\overset{\displaystyle O}{\|}}{C}—O—R—U]_pR'$$

in which

X is a hydrogen or halogen atom or a methyl group;
R is an alkylene or arylene group;
p is an integer and is 2 or 3 or 4 depending on the valency of R'; and
U is a urethane group of formula V or VIII

$$—N(Y)—\overset{\overset{\displaystyle O}{\|}}{C}—O—$$

or

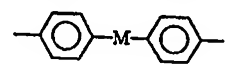
$$-O-\overset{\overset{\displaystyle O}{\|}}{C}-N(Z)-$$

in which

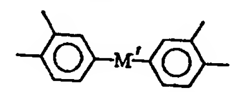
Y is hydrogen or an aryl group and

Z is hydrogen, an alkyl or an aryl group;

R′ is a divalent, trivalent or tetravalent group, the said divalent group being selected from alkylene groups of from 2 to 10 carbon atoms, phenylene groups, dimethyl-substituted phenylene groups, a diphenylene group, the group of formula XI



in which M is CH_2, O, S, SO_2, NH or $(CH_3)_2C$, divalent aliphatic groups containing one or two ether groups or an ester group, the said trivalent group being a trivalent aliphatic hydrocarbon group, and the said tetravalent group being a tetravalent aliphatic hydrocarbon group or the group of formula XII



where M′ is a methylene group or an oxygen atom: optionally the group R′ may be an oligomeric group of formula

$$R'''-[-U-R''-U-R''']_n$$

in which R″ is any one of the divalent groups defined hereinabove in respect of R′, U is as defined hereinabove, R‴ is one of the divalent or trivalent groups defined hereinabove in respect of R′, n is an integer of 1 to 5 when R‴ is divalent and n is 1 when R‴ is trivalent.

2. An oligourethanacrylate as claimed in Claim 1, having the formula

$$CH_2{=}CH{-}COOCH_2CH_2NHCOO(CH_2)_4OOCNHCH_2CH_2OOC{-}CH{=}CH_2$$

3. An oligourethanacrylate as claimed in Claim 1, having the formula

$$CH_2{=}C(CH_3){-}COOCH_2CH_2OOCNH(CH_2)_2NHCOOCH_2CH_2OOC{-}C(CH_3){=}CH_2$$

4. An oligourethanacrylate as claimed in Claim 1, having the formula

$$CH_2{=}C(CH_3){-}COOCH_2CH_2OOCNH(CH_2)_{10}NHCOOCH_2CH_2OOC{-}C(CH_3){=}CH_2$$

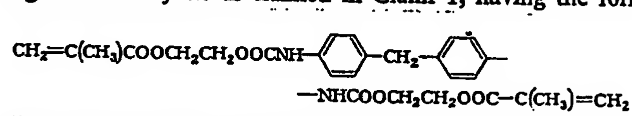
5. An oligourethanacrylate as claimed in Claim 1, having the formula

$$CH_2{=}C(CH_3)COOCH_2CH_2NHCOO(CH_2)_2O(CH_2)_2OOCNHCH_2CH_2OOC{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2$$

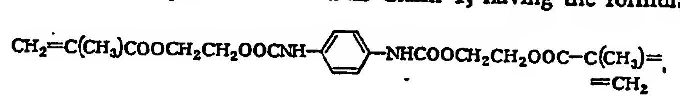
6. An oligourethanacrylate as claimed in Claim 1, having the formula

$$CH_2{=}C(CH_3)COOCH_2CH_2N(C_6H_5)COO(CH_2)_2$$
$$O(CH_2)_2OOCN(C_6H_5)CH_2CH_2OOC{-}C(CH_3){=}CH_2$$

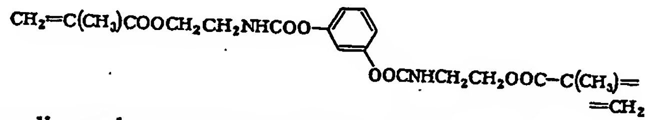
7. An oligourethanacrylate as claimed in Claim 1, having the formula



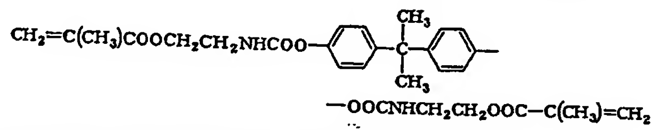
8. An oligourethanacrylate as claimed in Claim 1, having the formula



9. An oligourethanacrylate as claimed in Claim 1, having the formula



10. An oligourethanacrylate as claimed in Claim 1, having the formula



11. An oligourethanacrylate as claimed in Claim 1, having the formula

$$\begin{array}{l} \quad\quad\quad\;\; CH_2OOCNHCH_2CH_2OOC{-}C(CH_3){=}CH_2 \\ CH_3CH_2{-}C{-}CH_2OOCNHCH_2CH_2OOC{-}C(CH_3){=}CH_2 \\ \quad\quad\quad\;\; CH_2OOCNHCH_2CH_2OOC{-}C(CH_3){=}CH_2 \end{array}$$

12. An oligourethanacrylate as claimed in Claim 1, having the formula

$$CH_2{=}C(CH_3){-}COOCH_2CH_2OOCNH(CH_2)_2NHCOO(CH_2)_2O(CH_2)_2OOCNH(CH_2)_2{-}NHCOOCH_2CH_2{-}OOC{-}C(CH_3){=}CH_2$$

13. A method of preparing an oligourethanacrylate of general formula I defined in claim 1, comprising reacting a polyol polychloroformate with a telogen of formula IV, or reacting a polyamine with a telogen having the formula III

$$CH_2{=}C(X){-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl \qquad \text{III}$$

$$CH_2{=}C(X){-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R{-}N(Y)H \qquad \text{(IV)}$$

in which X, Y and R are as defined in claim 1, said reaction being carried out in organic solvent medium in the presence of a hydrogen chloride acceptor and at a temperature of from minus 10°C to the boiling point of the solvent.

14. A method as claimed in claim 13, in which the solvent is a mixture of water and an organic solvent and the temperature is room temperature.

15. A method as claimed in claims 13 or 14, in which the polyol polychloroformate is selected from the bis-chloroformates of propyleneglycol-1,3-butyleneglycol-1,4, pentamethyleneglycol-1,5, diethyleneglycol, hydroquinone, resorcinol, diphenylolpropane and polyoxypropyleneglycol having a molecular weight of 200, the trichloroformates of etriol and glycerol and the tetrachloroformate of pentaerythritol.

16. A method as claimed in claims 13, 14 or 15, in which the polyamine is selected from ethylenediamine, hexamethylenediamine, decamethylenediamine, n-phenylenediamine, 4,4′-diaminodiphenylmethane, 4,4′-diaminodiphenyloxide, 4,4′-diaminodiphenylsulphone, 3,3′,4,4′-tetraaminodiphenylmethane, and 3,3′,4,4′tetraaminodiphenyloxide.

17. A method as claimed in any one of claims 13 to 16, in which the telogen of formula III is selected from the chloroformate of a monoacrylate, monomethacrylate or monohaloacrylate of an alkyleneglycol or bis-phenol.

18. A method according to claim 17, in which the telogen of formula III is selected from the chloroformate of the monoacrylic, monomethacrylic or monohalo-acrylic ester of ethyleneglycol, diethylene glycol, triethyleneglycol, propyleneglycol-1,3: butyleneglycol-1,4: pentamethyleneglycol-1,5; diphenylolpropane, resorcinol or hydroquinone.

19. A method according to any one of claims 13 to 18 in which the telogen of

formula IV is a monoaminoalkyl acrylate or an N-aryl-substituted monoaminoalkyl acrylate containing not less than one hydrogen atom at the nitrogen atom.

20. A method according to claim 19, in which the telogen of formula IV is selected from 2-aminoethylacrylate, 2-aminoethylmethacrylate and 2-phenylaminoethylmethacrylate.

21. A method as claimed in any of claims 13 to 20, in which when R′ is R‴—[—U—R″—U—R‴]$_n$ the polyamine is an oligomer having terminal amino groups, the oligomer having been prepared by condensation of a polyamine with a polyol polychloroformate, the said polyol polychloroformate being either the bis-chloroformate of glycol or the bis-chloroformate of a bis-phenol and the ratio of the polyamine to the said bis-chloroformate being

$$\frac{n+1}{n}.$$

22. A method as claimed in any one of claims 13 to 20, in which when R′ is R‴—[—U—R″—U—R‴]$_n$ the polyol polychloroformate is an oligomer with a terminal chloroformate group, the oligomer having been prepared by condensation of a diamine with a polyol polychloroformate, the ratio of the diamine to the polyol chloroformate being

$$\frac{n}{n+1}.$$

23. A method as claimed in any one of claims 13 to 22, in which the reactants are taken in the stoichiometric ratio.

24. A method as claimed in any one of claims 13 to 23, in which the solvent is selected from chloroalkanes, nitroalkanes, benzene, homologues of benzene, and tetrahydrofuran.

25. A method as claimed in any one of claims 13 to 24, in which the hydrogen chloride acceptor is a tertiary amine, selected from trimethylamine, triethylamine, tributylamine, pyridine, homologues of pyridine, N,N-dimethylaniline, and N,N-diethylaniline.

26. A method as claimed in claim 14, in which the polyamine is in the form of its salt of an acid selected from HCL, HBr, and H_2SO_4.

27. A method as claimed in claim 14, in which the polyamine is in aqueous solution.

28. A method as claimed in claims 14 or 26 and 27, in which the hydrogen chloride acceptor is an inorganic alkaline agent selected from oxides of the alkali and alkaline earth metals, hydroxides of alkali and alkaline earth metals, carbonates of the alkali and alkaline earth metals.

29. A method as claimed in any one of claims 14 to 25, in which the process is carried out at a temperature of from minus 10°C to plus 80°C.

30. Polymers with reticulate structure on the basis of oligourethanacrylates as claimed in any one of claims 1 to 12.

31. A method for preparing oligourethanacryate substantially as hereinbefore described in Examples 1 to 26.

32. Oligourethanacrylates whenever prepared by the method claimed in any one of claims 13 to 29.

FITZPATRICKS,
Chartered Patent Agents,
14—18 Cadogan Street,
Glasgow, G2 6QW.
and
Warwick House,
Warwick Court,
London, WC1R 5DJ.

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